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The characteristics of torrefied microalgae

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ABSTRACT

In order to utilize microalgae and their residues as biomass solid fuels for co-firing in the existing pulverized coal-fired power plants, this study is to investigate the properties of fuels from those feedstock prepared by the torrefaction process. The microalgae were cultivated by using flue gas emitted from coal-fired power plants of Taipower Co., and the residue was from extraction of microalgae by hot water. The operating conditions for the torrefaction temperature and residence time were set as 200, 250, 300 and 350 °C, and 30, 60, 120 min, respectively. Also, 30 °C/min and 50 °C/min as the heating rates were chosen to examine the mass yield of solid torrefied biomass from microalgae. After torrefaction, the ultimate analysis, proximate analysis, and higher heating value analysis of the torrefied biomass were carried out. In addition, the Hardgrove Grindability Index (HGI) of microalgal residue and its torrefied solid were measured. The results show that carbon content, ash content, fixed carbon content, higher heating value, and HGI of torrefied biomass increased with increasing the operating temperature and residence time. At the condition of 300 °C and 30 min, the higher heating value of torrefied microalgae and microalgal residue were 25.92 MJ/kg and 26.76 MJ/kg, respectively. Compared to raw materials, the increases were 26.70% and 17.16%, respectively. At the same circumstances, hydrogen content, oxygen content, moisture content and mass yield of solid torrefied biomass decreased with increasing temperature and residence time. After torrefaction at 300 °C, the moisture content were all down to 1%, and the mass yield of solid torrefied biomass under 350 °C by torrefaction were also kept up to 50%. The HGI of torrefied microalgal residue was 48.53, which exceed the sub-bituminous coal when the operation condition temperature was up to 250 °C.

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1. Introduction

Nowadays, the climate change made from the greenhouse effect is getting worse and severely influencing the environment. The CO_2 emission from burning fossil fuels is increasing in a rate of 2.23% per year [1] and the increasing tendency is still ongoing. In order to stop the increase of CO_2 emission, the global study is orienting to develop the sustainable energy.

According to the statistical data [2], biomass energy is the fourth largest primary energy in the world that is only next to the oil, coal and natural gas. In order to obtain more supply of the sustainable energy, the development of biomass energy is an important work with no time to wait. In addition, over the way of converting biomass into clean biomass energy through thermochemical process, it will also make great effort on reducing the emission. Employing the raw biomass material as a fuel directly would cause several problems, such as its high moisture content, poor grindability and relatively lower heating value, which make raw biomass an high cost in transportation.

Recently, in order to improve the biomass property, torrefaction process is developed as a thermal pre-treatment technology when biomass turns into solid fuels, under the atmospheric pressure and absence of oxygen. Usually, the reaction temperature was between 200 and 300 °C, and the residence time was about 1hour. It can also improve the quality of solid fuels simultaneously.

The pyrolytic behavior in the torrefaction process is very complicated. Reaction rate, weight loss and torrefaction yield may vary because of variability in raw materials. Due to the wide varieties of biomass and the difference in major composition as well as thermal stability, it is essential to understand the pyrolytic characteristics for the raw material and torrefied biomass. Recently, there has been some research accomplishment in understanding the pyrolysis mechanism and kinetic behavior for the torrefaction process [3–7]. Chen and Kuo [3] employed a thermogravimetry to conduct torrefaction experiments for four different kinds of biomass and observed the variation in weight loss. They also carried out torrefaction of seven constituents contained in biomass including hemicellulose, cellulose, lignin, xylan, glucan, glucose and xylose, and classified three levels of torrefaction, light, mild and severe, based on different torrefaction temperatures [4]. In addition, Chen et al. [5] did not recommend for conducting biomass torrefaction at

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higher temperature, because the heating value of torrefied biomass increased with increasing the torrefaction temperature, but the product yield showed the contrary results. Prins et al. [6] and Chen and Kuo [7] established the parameters of biomass torrefaction kinetics through thermogravimetric analysis (TGA). It may also provide as references in designing the industrial torrefaction process.

In the aspect of fuel properties, torrefied biomass, compared to the raw materials, has lower water content, higher carbon content, higher heating value, and higher energy density. Structurally, due to the increase of hardness and brittleness, grinding property of torrefied biomass is also improved [8]. Chen et al. [9] also conducted torrefaction of biomass pellet and found that the particle size distribution was improved after grinding, and it could promote the applications of grinded biomass in blast furnaces and boilers.

At present, Taiwan Power Co. (TPC) employs fossil power as major local power supply, which uses the fossil fuels (petroleum (4.54%), coal (57.57%) and natural gas (37.89%)) to generate power [10]. Yet, CO_2 generated from the combustion of these fossil fuels will definitely impact the development of the future operation. Therefore, Taiwan Power Research Institute (TPRI) has been working on the study of using the exhaust gas emitted from fossil power units as carbon source to fix carbon dioxide by fast growth microalgae. Microalgae and microalgal residue are one of the biomass feedstock. Thus, employing microalgae and the residue as fuels for power generation can also contribute the goal of eco-friendly and zero CO_2 emission eventually. However, currently most power plants operated by Taiwan Power Co. are pulverized coal-fired boilers. It is difficult to co-fire coal with solid biomass fuels directly, except grinding biomass. On the other hand, to grind the solid biomass, the power plant must install a new grinding facility, and the cost should be increased. Therefore, if solid biomass could be blended with coal in the coal mill, pre-treatment of biomass, i.e., torrefaction, is a solution to improve the biomass fuel quality.

In this study, the microalgae and microalgal residue supplied by TPRI were employed to carry out the torrefaction experiments. After torrefaction, ultimate, proximate, mass yield, higher heating value, Hardgrove Grindability Index (HGI), and thermal gravimetric analyses were conducted to investigate characteristics of torrefied microalgae as a reference of co-firing fuels for the pulverized coal-fired power plants.

Table 1
Characteristics of feedstock.

Feedstock	MAR[b]	MA[b]
Ultimate analysis (wt.%, dry)		
C	50.53	45.70
H	7.40	7.71
O[a]	24.29	25.69
N	11.69	11.26
S	0.73	0.75
Proximate analysis (wt.%)		
Moisture content	4.19	7.61
Volatile matter	71.36	64.75
Fixed carbon	19.31	19.42
Ash	5.14	8.22
HHV_{wb} (MJ/kg)	22.84	20.46
HGI (–)	22.48	N/A

N/A: Not available.
[a] By difference.
[b] MAR: microalgal residue; MA: microalgae.

2. Materials and methods

The microalgae and microalgal residue used in this study were supplied by TPRI. The algae are *spirulina platensis*, and the proximate and ultimate analyses of microalgae and their residue are listed in Table 1. The operating conditions for the torrefaction temperature were set as 200 °C, 250 °C, 300 °C, and 350 °C. The residence times were 30 min, 60 min, and 90 min, respectively. Also, 30 °C/min and 50 °C/min as the heating rates were chosen to examine the mass yield of solid torrefied biomass from microalgae. The test code uses MA as the microalgae powder, and MAR as the microalgal residue. The number added after the code represents the heating rate (°C/min).

The torrefaction equipment is a batch multi-sectional temperature-controlled furnace as shown in Fig. 1. The furnace volume is about 15 L with a 20 cm × 20 cm × 5 cm perforated pan to carry the sample. For conducting a torrefaction experiment, the sample was placed into the torrefaction furnace, and nitrogen gas was injected into the furnace at the flowrate of 1 L/min to provide the oxygen-free atmosphere. The reaction was processed in four

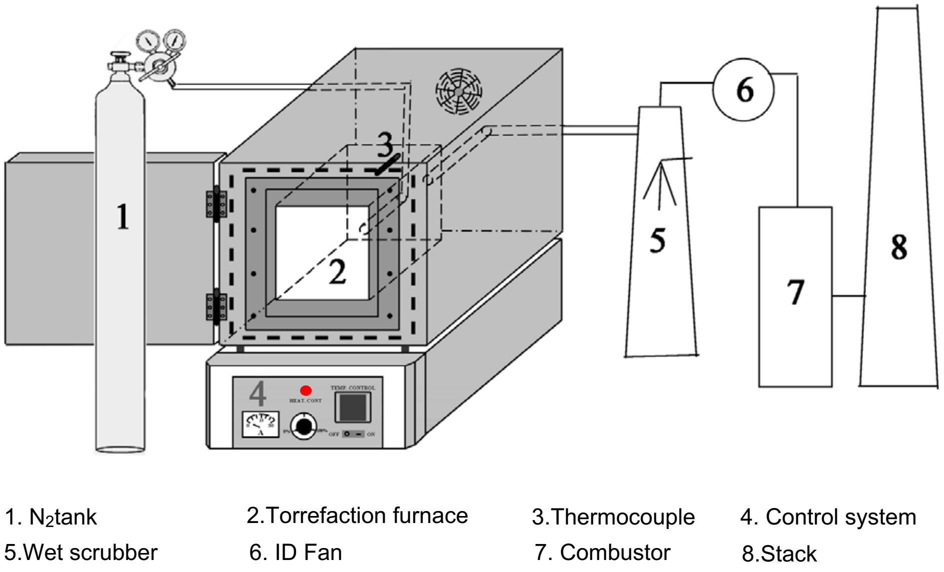


Fig. 1. Torrefaction equipment.

stages. In the first stage, the temperature was risen up to 105 °C within 30 min; in the second stage, the sample stayed at 105 °C for 30 min to remove the moisture; in the 3rd stage, the temperature was risen up to the required torrefied temperature; and in the 4th stage, the sample stayed at setting torrefied temperature for the setting residence time.

After torrefaction, the ultimate (Elementar vario EL), proximate, mass yield, higher heating value (Parr 6300 Calorimeter) and HGI (kER-60 HGI meter) analyses were conducted to investigate characteristics of the torrefied biomass. Also, thermal gravimetric analysis (TGA) was carried out in a thermogravimetric Analyzer (Perkinelmer, Simultaneous Thermal Analyzer, STA6000) to understand the torrefaction mechanism of the microalgae torrefaction.

3. Results and discussion

3.1. Mass yield of torrefied biomass

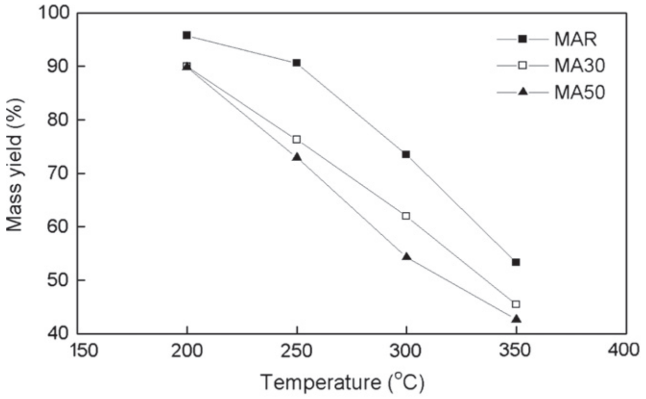
The effect of torrefaction temperature on the mass yield of torrefied biomass is shown in Fig. 2a. It can be found that the mass yield decreased with increasing the torrefaction temperature. The results are in agreement with the work by Pimchuai et al. [11]. Fig. 2b shows the effect of the residence time on the mass yield of torrefied biomass operated at 300 °C. Similarly, the mass yield decreased with increasing the residence time. Compared Fig. 2a and b, it can be seen that mass yield decreased fast from 200 °C to 350 °C at the same residence time, but it decreased more mitigative at the same torrefaction temperature. It can be concluded that the influence of temperature to mass yield is more important than residence time.

The heating rate also affects yield of torrefaction products. With comparison among yield at different heating rate, shown in Fig. 2a, it was found that maximum weight loss happened at 50 °C/min. Williams and Besler [12] mentioned that when hemicellulose was pyrolyzed at different heating rate, temperature shift could affect the kinetic behavior at higher heating rate, and the reaction favored transglycosylation and fragmentation, which would increase volatiles and decrease coke.

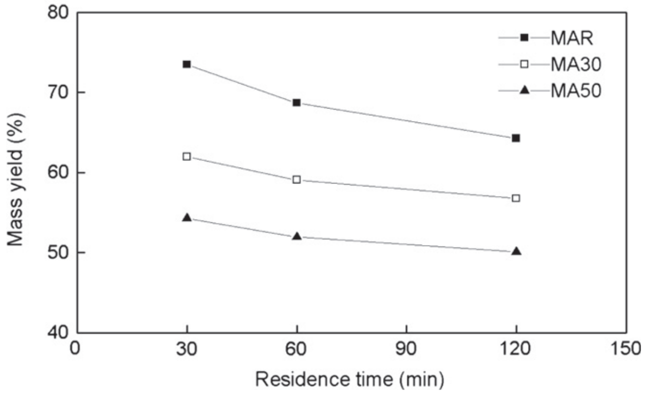
Several years ago, some scholars conducted thermal gravimetric analysis with microalgae and established its reaction kinetics for applications of raw microalgae feedstock to combustor directly [13,14]. Recently, there have been researches to investigate pyrolytic characteristics with thermal gravimetric analysis for microalgae that was subject to pyrolysis at different oxygen content [15]. In this study, the TGA and derivative thermogravimetric (DTG) curves for microalgae and microalgae residue are shown in Fig. 3 for understanding the torrefaction mechanism. It can be found that the pyrolysis of microalgae and microalgal residue includes three stages. The first stage appeared before 200 °C and was mainly the removal of moisture and light volatiles. The second stage was the primary thermal pyrolysis at 200–480 °C. At this stage, microalgae and the residue underwent severe devolatilization and generated a huge amount of volatiles. The maximum weight loss for microalgae and the residue happened at 325 and 330 °C. This is consistent with the condition that the yield was dramatically reduced to 50% at torrefaction temperature 350 °C shown in Fig. 2. The third stage appeared after 480 °C. The weight loss curve gradually went down and leveled off. At this stage, carbonaceous matters in solid residues underwent slower pyrolysis.

3.2. Proximate and ultimate analyses of torrefied biomass

The proximate analysis items include the moisture content, volatile, fixed carbon and ash content; ultimate analysis items include C, H, O, N, and S elements. The results of proximate analysis at different torrefaction temperatures are shown in Fig. 4. It can be seen that the moisture content decreased obviously with increasing temperature (Fig. 4a). After the temperature exceeded 300 °C, moisture content reduced below 1%. During the torrefaction process, hydroxyl group (–OH) of the biomass feedstock is destroyed, and the biomass losses the capability to form hydrogen bonds with water [16,17]. Thus, the torrefied biomass becomes hydrophobic. The ash content and fixed carbon increased with increasing temperature (Fig. 4b and c), but volatile shows the contrary results



(a) Residence time = 30 min



(b) Torrefaction temperature = 300°C

Fig. 2. The effect of torrefaction temperature and residence time on the mass yield of torrefied biomass.

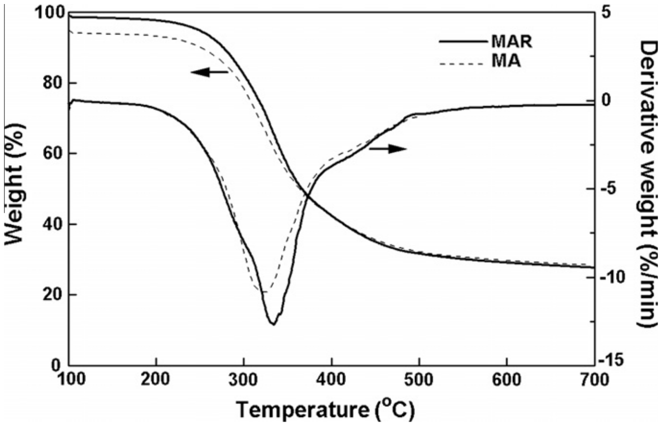
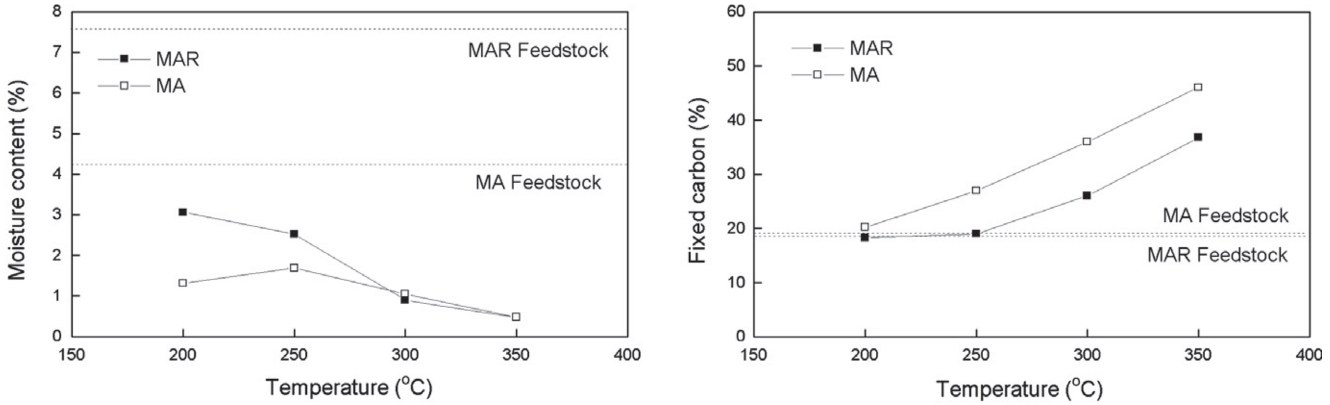
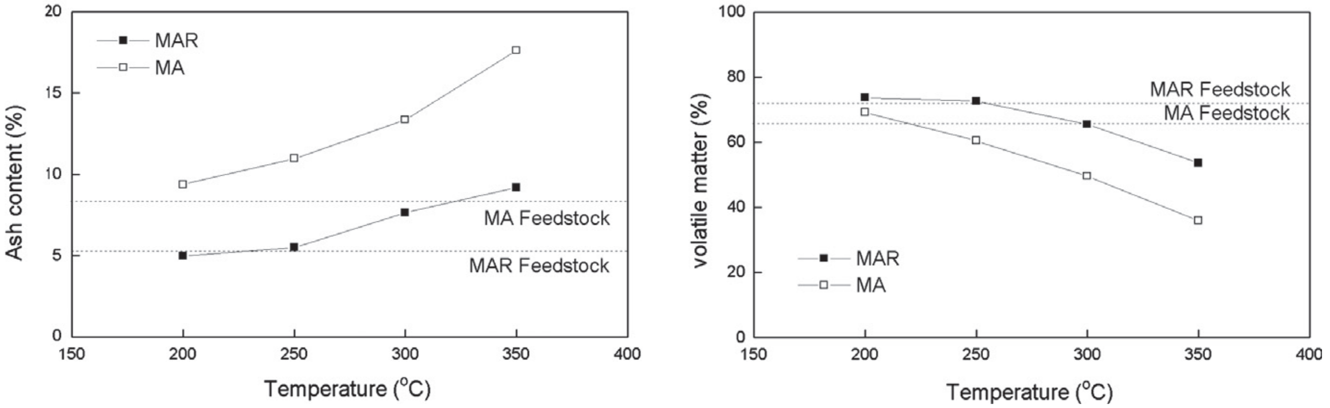


Fig. 3. The TGA and DTG diagrams of microalgae and microalgal residue by heating mode.



(a) Moisture

(c) Fixed carbon



(b) Ash content

(d) Volatile

Fig. 4. Effect of torrefaction temperature on torrefied biomass properties. (Residence time = 30 min).

(Fig. 4d). It is attributed to the weight loss. Volatile is combustible, but the fixed carbon and ash content are not changed at all.

Both moisture and ash are non-combustible. The existence of ash lowers the heating value of the solid fuel and affects fuel ignition and combustion. The high moisture content in the solid fuel also reduces combustor temperature. As for volatiles and the fixed carbon, both are combustible and contribute to the heating value. The ratio of volatiles to the fixed carbon is an indicator of the fuel quality. When the fixed carbon is higher, volatile is lower, less smoke is generated and less flame retardency is presented during combustion. As a result, the fuel quality is close to coal. Therefore, the increased fixed carbon and decreased volatiles after torrefaction raise the potential as a fuel being co-fired with coal or as a direct combustion fuel.

The results of the ultimate analysis at different torrefaction temperatures are shown in Fig. 5. In Fig. 5a and b, it is clear that the O and H contents in the torrefied biomass decreased with increasing temperature, but C content shows the contrary results, and it can be seen in Fig. 6. Those are in agreement with the work of Arias et al. [18] and Bridgeman et al. [19]. It supports the theorem mentioned above that the decrease of moisture content is from the remove of bonded H_2O in the feedstock, because the hydroxyl group (–OH) of the biomass feedstock has been destroyed.

Fig. 7 shows the van Krevelen's diagram [20], when atomic H/C respect to atomic O/C is plotted. It can be found that H/C and O/C values decreased gradually with increasing temperature and residence time. After torrefaction, the property of biomass feedstock is approaching to coal. Bridgeman et al. [19] mentioned that a large amount of elements released from torrefaction are O and H, thus the H and O contents in biomass gradually decreased. Yet, from the work of Bergman et al. [16], the decrease of O/C and H/C can reduce the thermodynamic loss of smoke and vapor from excessive oxidation. Therefore, torrefied biomass has the potential in the application of co-firing with coal.

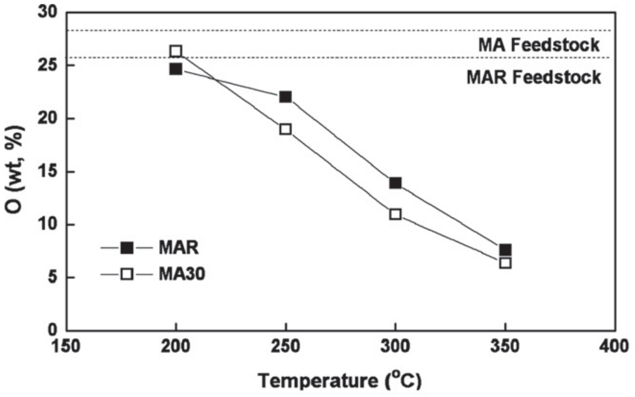
3.3. Higher heating value of torrefied biomass

The effects of the torrefaction temperature and residence time on the higher heating value (HHV) of torrefied biomass are shown in Fig. 8. It can be found that the HHV increased with increasing temperature and residence time. While torrefaction of microalgae and microalgal residue were carried out at 300 °C with a residence time of 30 min, the HHV were up to 26.76 MJ/kg and 25.92 MJ/kg, respectively.

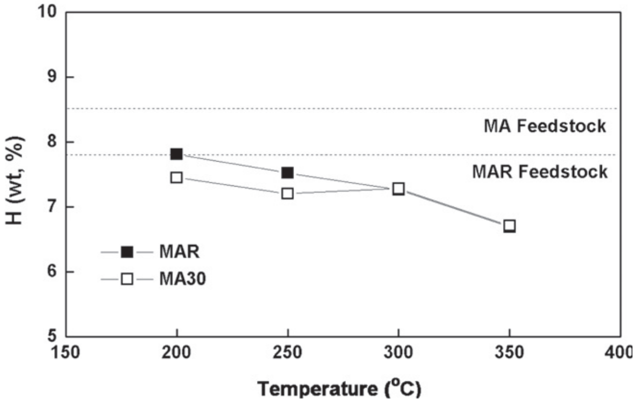
Chen and Kuo [4] indicated that during the torrefaction process, the oxygen in the feedstock is consumed. Thus the C–O bonds in woody biomass decreased. Since the C–C bond energy is higher than that of the C–O bond, therefore, the carbon content increases and causes the uprising of the heating value with increasing temperature and residence time. Also, after torrefaction, because the generation of CO_2 and H_2O decreased, the efficiency of applying torrefied biomass can be enhanced.

3.4. Hardgrove grindability index of torrefied biomass

As mentioned above, it is difficult to co-fire coal with solid biomass fuels directly in a pulverized coal-fired power plant without installing a new biomass grinding facility. To blend with coal in a coal mill directly, biomass must be easy to be grinded. The Hardgrove Grindability Index (HGI) is an indicator to check the grinding



(a) O content



(b) H content

Fig. 5. Effect of torrefaction temperature on O and H contents. (Residence time = 30 min).

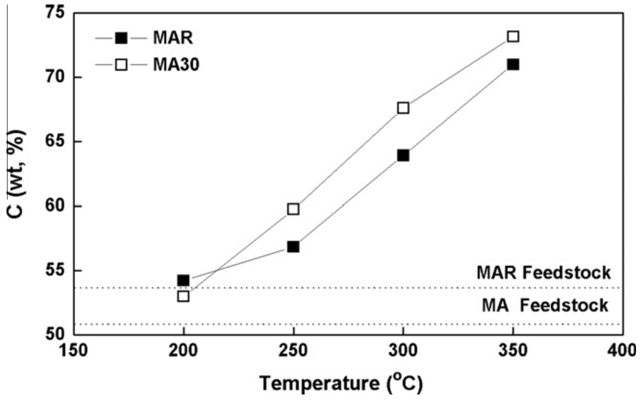
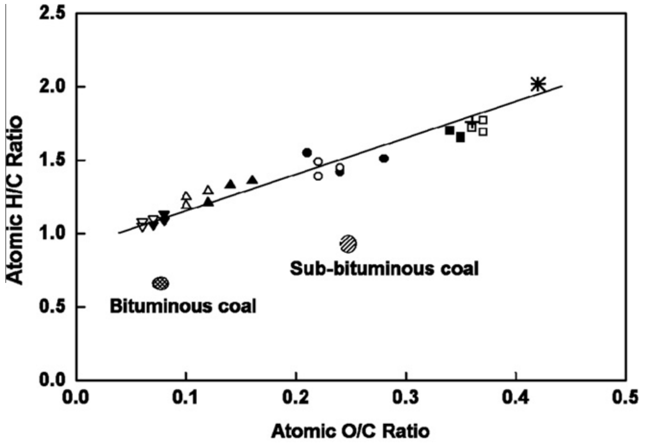
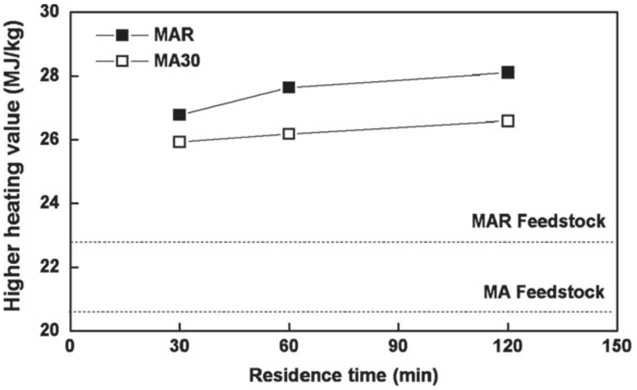


Fig. 6. Effect of torrefaction temperature on C contents. (Residence time = 30 min).

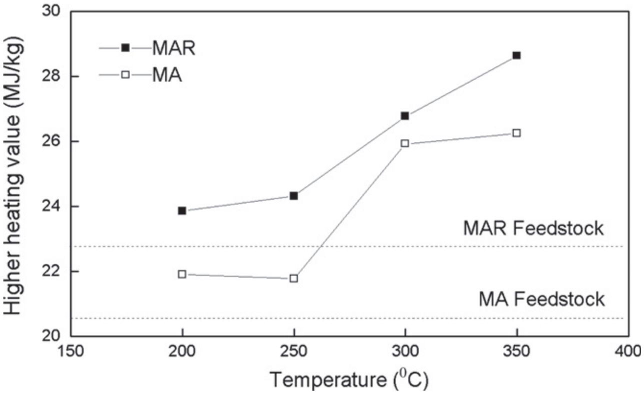


	Feedstock	T200	T250	T300	T350
MAR	+	■	●	▲	▼
MA	✳	□	○	△	▽

Fig. 7. van Krevelen's diagram for microalgae (MA) and microalgal residue (MAR) torrefied biomass.



(a) Torrefaction temperature = 300°C



(b) Residence time = 30 min

Fig. 8. Effect of torrefaction temperature and residence time on higher heating value of torrefied biomass.

scale of coal for a coal mill. HGI represents the difficulty for grinding solid sample into the powder, and higher HGI value means easier to grind the sample into powder. Therefore, if solid biomass would be blended with coal in the coal mill for applications in a pulverized coal-fired power plant, its HGI should be not less than that of coal.

After the extraction process, microalgal residue is the rock-like solid, not the powder. For utilizing microalgal residue as fuels for co-firing in the existing pulverized coal-fired power plants, microalgal residue should be pre-treated to meet the grinding quality of coal in the coal mill. Fig. 9 shows the effect of temperature and residence time on HGI for torrefied microalgal residue. The HGI of raw microalgal residue and sub-bituminous coal were 22.48 and 48.53, respectively. It can be seen that the HGI increased with increasing the temperature and residence time. The HGI of torrefied microalgal residue can exceed the sub-bituminous coal when the operation temperature was up to 250 °C.

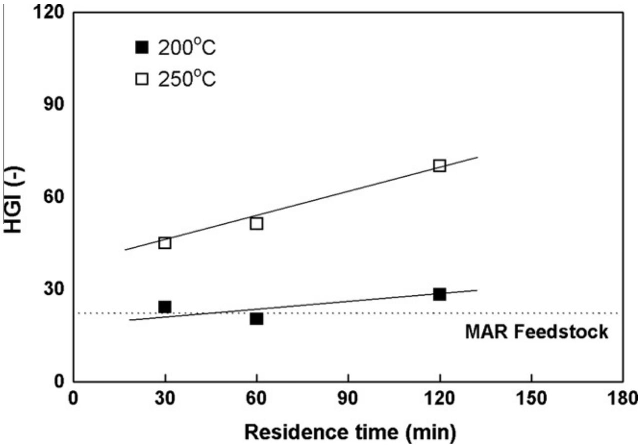


Fig. 9. Effect of residence time on HGI of torrefied microalgal residue.

In general, besides structural depolymerization there is a rearrangement phenomenon during biomass thermal pyrolysis. With increasing reaction temperature, the biomass is toward carbonization obviously, and becomes increasingly hard and brittle. Therefore the grinding property of torrefied biomass is improved. However, microalgae lack the lignin that is contained in woody biomass for support and protection. Among microalgae species, *spirulina platensis* is multicellular organisms without the sheath or specialized cells, such as heterocyst and akinetes. Its cell wall is thin and mainly comprises peptidoglycan, so it is easily affected and damaged by external force or heating, and therefore its grinding property is further affected.

Therefore, after torrefaction, the torrefied microalgal residue has greatly upgraded the grinding property, which can be blended with coal directly for co-firing in the existing pulverized coal-fired power plants.

4. Conclusions

In this study, torrefaction of microalgae and microalgal residue have been carried out in a 15-L batch multi-stage temperature-controlled torrefaction furnace. The results show that carbon content, ash content, fixed carbon content, higher heating value and HGI of torrefied biomass increased with increasing the operating torrefaction temperature and residence time. At the condition of 300 °C and 30 min, the higher heating value of torrefied microalgae and microalgal residue were 25.92 MJ/kg and 26.76 MJ/kg, respectively. Compared to raw materials, the increases were 26.70% and 17.16%, respectively. At the same circumstances, the carbon contents also increased by 27.94% and 8.86%. Hydrogen content, oxygen content, moisture content and mass yield of solid torrefied biomass decreased with increasing temperature and residence time. After torrefaction at 300 °C, the moisture content were all down to 1%, and the mass yield of solid torrefied biomass under 350 °C by torrefaction were also kept up to 50%. The HGI of torrefied microalgal residue was 48.53, which exceed the sub-bituminous coal when the operation condition temperature was up to 250 °C.

Therefore, after torrefaction, the torrefied microalgal residue has greatly upgraded the grinding property, which can be blended with coal directly for co-firing in the existing pulverized coal-fired power plants, i.e., the fuel quality of torrefied biomass is close to coal.

Acknowledgment

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